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LABORATORY PROCEDURE FOR THE SPECTROPHOTOFLUOROMETRIC DETERMINATION OF SELENIUM IN SOLID WASTE

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The determination of selenium in solid waste and the effluents of solid waste treatment systems is of considerable interest because of the toxicity of selenium and its reported presence in almost all conceivable types of paper. A 2,3-diaminonaphthalene (DAN) analytical procedure is preceded by isolation of selenium with toluene 3,4-dithiol and includes the use of EDTA, sodium fluoride and sodium oxalate masking agents. The reactions in the procedure are thought to involve the formation of a piazselenol. he piazselenol emits at 5700 A when excited at 3170 A.

The use of the DAN fluorometric procedure affords the sensitivity necessary for trace analysis while retaining a precision of measurement comparable to competitive methods. The isolation step and masking agents are used to prevent background fluorescence and foreign ion effect.

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written by
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U.S. ENVIRONMENTAL PROTECTION AGENCY
Solid Waste Management Office
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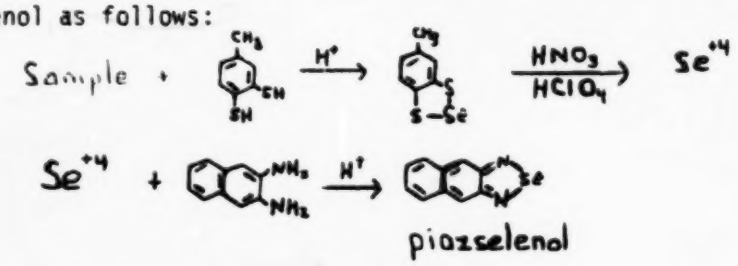
DISCUSSION

The determination of selenium in solid waste and the effluents of solid waste treatment systems is of considerable interest because of the toxicity of selenium and its reported presence in almost all conceivable types of paper. A 2,3-diaminonaphthalene (DAN) analytical procedure is preceded by isolation of selenium with toluene 3,4-dithiol and includes the use of EDTA, sodium fluoride and sodium oxalate masking agents. The reactions in the procedure are thought to involve the formation of a piazselenol as follows:



The piazselenol emits at 570 mμ when excited at 317 mμ.

The use of the DAN fluorometric procedure affords the sensitivity necessary for trace analysis while retaining a precision of measurement comparable to competitive methods. The isolation step and masking agents are used to prevent background fluorescence and foreign ion effect.

APPARATUS AND INSTRUMENTS

The apparatus required for the analyses is:

1. Farrand Mark I Spectrofluorometer with 10mm slits and RCA IP 121 phototube
2. Wiley Mill fitted with a 10 mesh screen

3. Parr bomb calorimeter
4. Beckman zeromatic pH meter
5. Sorval SS-1 centrifuge

REAGENTS

The analysis requires the following reagent grade chemicals:

1. Hydrochloric acid
2. Sodium hydroxide
3. Nitric acid
4. 72% Perchloric acid
5. Ethylene chloride
6. Carbon tetrachloride
7. Cyclohexane
8. 2,3-diaminonaphthalene (DAN) (Aldrich Chemical Co.)
9. Toluene-3,4-dithiol zinc salt (Eastman Organic Chemicals)
10. Sodium fluoride
11. Sodium oxalate ($Na_2C_2O_4$)
12. Sodium selenite (Na_2SeO_3)
13. Ethylenediaminetetracetic acid disodium salt (EDTA)
14. Sulfuric acid
15. Quinine

Prepare solutions of the above reagents as follows:

1. Prepare 0.1N HCl by diluting 8.3 ml of concentrated HCl to 1000 ml with distilled water.
2. Prepare 0.1N NaOH by dissolving 4.0 gm of NaOH in 1000 ml of distilled water.
3. Dissolve 480 gm of NaOH in 1000 ml of distilled water to produce an apprimately 12N solution.
4. Prepare 0.1% DAN fresh daily by dissolving 0.1 gm of DAN in 100 ml of 0.1N HCl.
5. Prepare a suitable dithiol solution fresh daily by adding 1 gm of toluene-3,4-dithiol zinc salt to several ml of ethanol. Add several drops of concentrated HCl and heat the mixture under the tap to produce a clear solution. Finally dilute the solution to 100 ml with ethanol.
6. Prepare 0.1M soldium fluoride by dissolving 4.2 gm in 1000 ml of distilled water.
7. Prepare 0.1M sodium oxalate by dissolving 13.4 gm in 1000 ml of distilled water.
8. Prepare 0.1M EDTA by dissolving 37.2 gm in 1000 ml of distilled water.
9. Prepare a standard solution of selenium by dissolving 0.2190 gm of Na_2SeO_3 in 1000 ml of distilled water. The concentration of this solution is 1000 μg Se/ml.

10. Dilute 2.8 ml of concentrated H_2SO_4 to 1000 ml thus producing a 0.1N solution.

11. Prepare a stock standard of quinine sulfate by dissolving 0.0100 gm of quinine in 1000 ml of 0.1N H_2SO_4 thus producing a concentration of 10 µg/ml. Prepare a working standard by diluting 1 ml of stock standard to 10 ml with 0.1N H_2SO_4. These solutions should remain in the dark when not in use.

SAFETY PRECAUTIONS

Adequately ventilate the spectrofluorometer lamp housing (with a hood if possible) because ozone is produced when the instrument is in use.

Take extreme caution during the nitric-perchloric acid digestions. These should never be taken to dryness because salts of perchloric acid are explosive.

Follow the manufacturer's instructions when using the Parr bomb and follow general laboratory safety practices at all times.

SAMPLE PREPARATION

Grind, mix and dry refuse and compost as described in an earlier chapter. Pelletize one gram samples and ash in a Parr bomb using 10 to 15 ml of water as absorbing solution under 30 atm. of oxygen pressure. Tap cool the bomb for 10 minutes and release the excess oxygen over a 2-minute period. Filter the bomb contents and washings through Whatman #12 filter paper and adjust the volume to 25 ml.

Place glass fiber millipore filters containing particulates, collected by isokinetic stack sampling, in a 100 ml beaker and add 15 ml of a 10:1 HNO and HClO acid mixture. Heat the mixture cautiously to remove oxides of nitrogen. After adding 25 ml of water, bring the solution to a boil, allow to cool and pass through a sintered glass filter. Adjust the volume to 50 ml. Extract samples (1 gm) of incinerator residue in the same manner.

PROCEDURE

1. Transfer 25 ml or an aliquot containing not less than 0.01 ug of Se into a 125 ml separatory funnel, adjust the volume to 35 ml and add 50 ml of conc. HCl.
2. Add 4 ml of freshly prepared 1% zinc dithiol suspension in ethanol. Mix and let stand 15 minutes.
3. Extract consecutively with a 10 ml mixture of ethylene chloride and carbon tetrachloride (1:1) and combine the organic phases in a stoppered test tube.
4. Add 1 ml of 72% $HClO_4$ and 10 drops of conc. HNO_3 and boil off organic solvent in boiling water bath.
5. Heat cautiously to fumes of $HClO_4$. Add 1 ml of H_2O, heat to fumes of $HClO_4$ again and add 10 ml of H_2O.
6. Adjust the pH to 2 with NaOH and add 0.5 ml each of 0.1M aqueous solutions of EDTA, NaF and $Na_2C_2O_4$.
7. Readjust the pH to 2 with HCl and add 4 ml of freshly prepared 0.1% DAN in 0.1N HCl.
8. Place the tubes in a 50°C H_2O bath for 20 minutes and tap cool.
9. Transfer contents of tubes to 125 ml separatory funnels containing 10 ml of cyclohexane. Extract and collect organic phase in a centrifuge tube.

10. Centrifuge at 2000 r.p.m. for 2 minutes and read on spectrophotofluorometer exciting at 370 mu and emitting at 517 mu.

STANDARDIZATION AND CALIBRATION

Prepare a calibration curve by analyzing standard solutions ranging from 0.005 to 1.0 µg Se. A linear relationship should be obtained by plotting the concentration of selenium versus the fluorescent intensity. A distilled water blank should give negligible readings at the analytical wave lengths. Bracket each sample reading by readings of 1 µg/ml guinine sulfate solution to account for fluctuations in lamp intensity.

CALCULATIONS

The formula needed to calculate the concentration of selenium in samples is:

$$C = (MM \times T_s)\ (S) \left(\frac{MM \times T_{Qc}}{MM \times T_{Qs}}\right) \left(\frac{10}{V_s}\right)$$

Where C = concentration of selenium in 10 ml cyclohexane

MM = meter multiplier setting

T_s = % transmittance of the sample

S = slope of the calibration curve

T_{Qc} = % transmittance of quinine for the calibration curve

T_{Qs} = % transmittance of quinine for the sample run

V_s = volume of sample analyzed

METHOD EVALUATION

Eleven samples of standard solution containing 1 µg of selenium per 10 ml of test solution were analyzed over a two day period. The results from these runs gave a standard deviation of 0.078 and a relative error of 2.57%. The standard deviation indicates ± 0.03 µg of selenium for the analyses of 1 µg standard solutions.

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